

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 1 101 736 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
23.05.2001 Bulletin 2001/21

(51) Int Cl.7: **C01G 49/00, H01F 1/34**

(21) Application number: **00125415.0**

(22) Date of filing: **20.11.2000**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: 19.11.1999 JP 32993799

(71) Applicant: **MINEBEA CO., LTD.**  
**Kitasaku-gun, Nagano-ken (JP)**

(72) Inventors:  
• **Kobayashi, Osamu, c/o Minebea Co., Ltd.**  
**Iwata-gun, Shizuoka-ken (JP)**

• **Yamada, Osamu, c/o Minebea Co., Ltd.**  
**Iwata-gun, Shizuoka-ken (JP)**  
• **Ito, Kiyoshi, c/o Minebea Co., Ltd.**  
**Iwata-gun, Shizuoka-ken (JP)**

(74) Representative: **Patentanwälte**  
**Schaad, Balass, Menzl & Partner AG**  
**Dufourstrasse 101**  
**Postfach**  
**8034 Zürich (CH)**

(54) **Mn-Zn ferrite and production thereof**

(57) This invention provides a Mn-Zn ferrite which has a high electrical resistance and can sufficiently satisfy the use in a high frequency region exceeding 1 MHz. This invention further provides a production process of the Mn-Zn ferrite in which mixed powder whose components are adjusted so as to have a basic component

composition containing 44.0 to 50.0 mol% Fe<sub>2</sub>O<sub>3</sub>, 4.0 to 26.5 mol% ZnO, 0.1 to 8.0 mol% one or two from TiO<sub>2</sub> and SnO<sub>2</sub> and the remainder consisting of MnO, and further to contain 0.01 to 2.00 mass% one or more of CoO, NiO, and MgO as additive is pressed, then sintered and cooled in the air or in an atmosphere containing some amount of oxygen.

**EP 1 101 736 A1**

## Description

BACKGROUND OF THE INVENTION

## 1. Field of the Invention

[0001] The present invention relates to an oxide magnetic material having soft magnetism, particularly to a Mn-Zn ferrite and more particularly to a Mn-Zn ferrite suitable for use as a high permeability material used for various inductance elements, impedance elements for EMI countermeasure or the like, a low loss material used for switching power transformers, an electromagnetic wave absorbing material and the like, and a production process thereof.

## 2. Description of the Related Art

[0002] A Mn-Zn ferrite is counted among the typical oxide magnetic materials having soft magnetism. The Mn-Zn ferrite of the prior art usually has a basic component composition containing more than 50 mol% (52 to 55 mol% on the average)  $\text{Fe}_2\text{O}_3$ , 10 to 24 mol% ZnO and the remainder consisting of MnO. And the Mn-Zn ferrite is usually produced by mixing the respective material powders of  $\text{Fe}_2\text{O}_3$ , ZnO and MnO in a prescribed ratio, subjecting to the respective steps of calcination, milling, component adjustment, granulation, pressing and the like to obtain a desired shape, then conducting sintering treatment in which the resulting product is kept at 1200 to 1400°C for 3 to 4 hours in a reducing atmosphere in which a partial pressure of oxygen is limited to a low level by supplying nitrogen. Incidentally, the reason why the Mn-Zn ferrite is sintered in the reducing atmosphere is that when it contains  $\text{Fe}_2\text{O}_3$  exceeding 50 mol% and is sintered in the air, densification is not attained sufficiently thereby failing to obtain excellent soft magnetism, and that although  $\text{Fe}^{2+}$  formed by the reduction of  $\text{Fe}^{3+}$  has positive crystal magnetic anisotropy and cancels negative crystal magnetic anisotropy of  $\text{Fe}^{3+}$  thereby enhancing soft magnetism, such a reducing reaction cannot be expected if sintering is conducted in the air.

[0003] Incidentally, it has been known that the above-mentioned densification depends on the partial pressure of oxygen in the temperature rise at the time of sintering and the above mentioned formation of  $\text{Fe}^{2+}$  depends on the oxygen concentration in the temperature fall after sintering, respectively. Therefore, when the setting of the partial pressure of oxygen at the time of sintering is wrong, it becomes difficult to ensure an excellent soft magnetism. Thus, in the prior art, the following expression (1) was experimentally established and the partial pressure of oxygen at the time of sintering has been conventionally controlled strictly in accordance with this expression (1).

$$\log P_{\text{O}_2} = -14540/(T + 273) + b \quad (1)$$

where T is temperature (°C),  $P_{\text{O}_2}$  is a relative partial pressure of oxygen, where  $P_{\text{O}_2} = P'_{\text{O}_2}/P_{\text{total}}$ ,  $P'_{\text{O}_2}$  is the absolute partial pressure of oxygen (Pa), and  $P_{\text{total}}$  is the total pressure (Pa), and b is a constant. The constant b has been set at about 7 to 8. The fact that the constant b is set 7 to 8 means that the partial pressure of oxygen during sintering must be controlled at a narrow range, which makes the sintering treatment very troublesome thereby increasing the production costs.

[0004] On the other hand, when the Mn-Zn ferrite is used as a magnetic core material, eddy current flows at a higher frequency region, resulting in a larger loss. Therefore, to extend an upper limit of the frequency at which the Mn-Zn ferrite can be used as a magnetic core material, its electrical resistance must be set as high as possible. However, the electrical resistance in the above-mentioned usual Mn-Zn ferrite has values smaller than 1  $\Omega\text{m}$  due to the transfer of electrons between the above-mentioned  $\text{Fe}^{3+}$  ions and  $\text{Fe}^{2+}$  ions and a frequency which is available for application is limited to about several hundred kHz maximum. Thus, in a frequency region exceeding this limit, permeability (initial permeability) is remarkably lowered and the properties of the soft magnetic material are lost.

SUMMARY OF THE INVENTION

[0005] The present invention has been made in consideration of the above-mentioned conventional problems. The present invention has objects to provide a Mn-Zn ferrite which has a high electrical resistance and can sufficiently satisfy applications in a high frequency region exceeding 1 MHz, and to provide a production process thereof in which such Mn-Zn ferrite can be obtained easily and at low costs.

[0006] The present inventors recognized in a series of researches related to the Mn-Zn ferrite that even if  $\text{Fe}_2\text{O}_3$  content is limited to 50.0 mol% or less, the Mn-Zn ferrite has a high electrical resistance by allowing suitable amounts of  $\text{TiO}_2$  and/or  $\text{SnO}_2$  to be contained and further a suitable amount of CuO to be contained as desired and can sufficiently

satisfy applications in a high frequency region exceeding 1 MHz, and have already disclosed the above in Japanese Patent Application No. Hei 11-29993 and Japanese Patent Application No. Hei 11-29994 (both applications are unpublished).

[0007] The inventions in the above-mentioned applications filed are made under the conviction that  $\text{Fe}^{2+}$  can be formed by allowing the Mn-Zn ferrite to contain Ti and/or Sn even when the Mn-Zn ferrite is sintered in the air or in an atmosphere containing some amount of oxygen, which is derived from the findings that iron components in the Mn-Zn ferrite exist as  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  and that Ti and Sn receive electrons from this  $\text{Fe}^{3+}$  to form  $\text{Fe}^{2+}$ . Further, in the inventions of the above-mentioned filed applications, the content of  $\text{TiO}_2$  and/or  $\text{SnO}_2$  in the basic component composition is limited to 0.1 to 8.0 mol% for controlling the amount of  $\text{Fe}^{2+}$  formed so that the coexistence ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  is optimized to offset positive and negative crystal magnetic anisotropy, whereby an excellent soft magnetism can be obtained. Further, since a number of  $\text{Ti}^{4+}$  and  $\text{Sn}^{4+}$  ions which have stable valences exist under the conditions, even if  $\text{Fe}_2\text{O}_3$  content is limited to a low level, an exchange of electrons between  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  is substantially blocked. Thus, an electrical resistance remarkably higher (about  $10^3$  times) than conventionally can be obtained.

[0008] The present inventors have made the invention by finding out in a series of researches related to the Mn-Zn ferrite that the initial permeability, particularly the initial permeability in a high frequency region is further enhanced by allowing one or more from CoO, NiO and MgO to be contained in a suitable amount as additive to a basic component composition in which  $\text{Fe}_2\text{O}_3$  content is limited to 50.0 mol% or less and in which  $\text{TiO}_2$  and/or  $\text{SnO}_2$  is contained in a suitable amount as described above.

[0009] That is, a Mn-Zn ferrite according to one aspect of the present invention to attain the above-mentioned objects is characterized in that the basic component composition contains 44.0 to 50.0 mol%  $\text{Fe}_2\text{O}_3$ , 4.0 to 26.5 mol% ZnO, 0.1 to 8.0 mol% one or two from  $\text{TiO}_2$  and  $\text{SnO}_2$  and the remainder consisting of MnO, and further contains 0.01 to 2.00 mass% one or more from CuO, NiO and MgO as additive.

[0010] Further, a Mn-Zn ferrite according to another aspect of the present invention is characterized in that the basic component composition contains 44.0 to 50.0 mol%  $\text{Fe}_2\text{O}_3$ , 4.0 to 26.5 mol% ZnO, 0.1 to 8.0 mol% one or two from  $\text{TiO}_2$  and  $\text{SnO}_2$ , 0.1 to 16.0 mol% CuO and the remainder consisting of MnO, and further contains 0.01 to 2.00 mass% one or more from CoO, NiO and MgO as additive.

[0011] The Mn-Zn ferrite according to the present invention is characterized in that  $\text{Fe}_2\text{O}_3$  content is limited to 50.0 mol% or less as described above. However, since too little  $\text{Fe}_2\text{O}_3$  content leads to reduction in the saturation magnetization or initial permeability, at least 44.0 mol%  $\text{Fe}_2\text{O}_3$  is adapted to be contained.

[0012] ZnO affects the Curie temperature and saturation magnetization. If ZnO is contained in a significant amount, the Curie temperature is lowered, resulting in practical problems. On the other hand, if ZnO is contained in too small an amount, the saturation magnetization is reduced. Thus, ZnO content is preferably controlled to the above-mentioned range of 4.0 to 26.5 mol%.

[0013] CuO has an effect to enable the Mn-Zn ferrite to be sintered at a low temperature. However, if the CuO content is too small, the effect is small. On the other hand, if the CuO content is too large, the initial permeability is reduced. Thus, CuO content is preferably controlled to the above-mentioned range of 0.1 to 16.0 mol%.

[0014] Since all of CoO, NiO and MgO are metal oxides having magnetism, they are solid-dissolved in the spinel lattices of the Mn-Zn ferrite and impart good influences to the magnetostriction, crystal magnetic anisotropy, and induced magnetic anisotropy, respectively. However, if their content is small, the effect is small. On the other hand, if their content is too large, the reduction of the initial permeability occurs. Thus, CoO, NiO or MgO content is preferably controlled to the above-mentioned range of 0.01-2.00 mass%.

[0015] Since in the Mn-Zn ferrite according to the present invention,  $\text{Fe}_2\text{O}_3$  content is limited to 50 mol% or less as described above, even if the Mn-Zn ferrite is sintered in the air or in an atmosphere containing some amount of oxygen, densification is sufficiently attained and desired soft magnetism can be obtained.

[0016] That is, a production process according to one aspect of the present invention to attain the above-mentioned objects is characterized in that mixed powder whose components are adjusted so as to compose the above-mentioned Mn-Zn ferrite is pressed, then sintered and cooled in the air.

[0017] Further, a production process according to another aspect of the present invention is characterized in that mixed powder whose components are adjusted so as to compose the above-mentioned Mn-Zn ferrite is pressed, then sintered and cooled in an atmosphere with the partial pressure of oxygen obtained by using an optional value in a range of 6 to 21 as the constant b in the aforementioned expression (1).

[0018] In this case, when a value larger than 21 is selected as the constant b in the expression (1), the resulting atmosphere becomes substantially the same as the air. Thus, it makes no sense to define the partial pressure of oxygen. Further, if this constant b is smaller than 6, electrical resistance becomes too low, whereby initial permeability at a high frequency is deteriorated.

## DETAILED DESCRIPTION OF THE INVENTION

[0019] In the production of a Mn-Zn ferrite, raw material powders of  $\text{Fe}_2\text{O}_3$ , ZnO,  $\text{TiO}_2$  and/or  $\text{SnO}_2$ , CuO, MnO and the like used as main components are previously weighed to match the above defined basic component composition, and are mixed. Then, the mixed powder is calcined and finely milled as required. The calcining temperature is slightly different depending upon the target composition, and an appropriate temperature can be selected within a range of 800 to 1000°C. A general-purpose ball mill can be used for fine milling of the mixed powder. Further, powder of CoO, NiO or MgO is added to the fine mixed powder in a prescribed amount (0.01 to 2.00 mass%) as the additive and mixed to obtain mixed powder having the target composition. Then, the mixed powder is granulated and pressed in accordance with a usual ferrite production process, and sintered at 900 to 1400°C. Incidentally, a process of adding a binder such as polyvinyl alcohol, polyacrylamide, methyl cellulose, polyethylene oxide, glycerin, or the like can be used for the granulation, and a process of applying pressure of, for example, 80 MPa or more can be used for the pressing.

[0020] The above-mentioned sintering and cooling after the sintering can be conducted in the air or in an atmosphere with the partial pressure of oxygen defined based on the aforementioned expression (1) where the constant b is within a range of 6 to 21. However, when they are conducted in an atmosphere containing oxygen, it is desirable to control the partial pressure of oxygen by allowing an inert gas such as nitrogen or the like to flow into a sintering furnace. In this case, an optional value in a wide range of 6 to 21 can be selected as the constant b given in the expression (1). Therefore, the control of the partial pressure of oxygen can be made easily.

[0021] Since the Mn-Zn ferrite thus obtained contains  $\text{TiO}_2$  and/or  $\text{SnO}_2$  as main components while containing 50 mol% or less  $\text{Fe}_2\text{O}_3$ , electrical resistance is remarkably increased (about  $10^3$  times) as compared to conventional Mn-Zn ferrite.

[0022] Further, generally, the limit of the initial permeability  $\mu$  in soft magnetic ferrite is inversely proportional to a frequency f (MHz) at which the ferrite is used, and is estimated with a value obtained by the expression (2) given below, but since the Mn-Zn ferrite according to the present invention contains CoO, NiO or MgO as additive in a prescribed amount, an initial permeability  $\mu$  of about 2000 at 1 MHz or about 200 at 10 MHz can be obtained as estimated. Thus, the present Mn-Zn ferrite can be ideal for use in a magnetic core material and an electromagnetic wave absorbing material for a high frequency exceeding 1 MHz.

$$\mu = K/f \quad (K = 1500 \text{ to } 2000) \quad (2)$$

## EXAMPLES

## Example 1

[0023] A mixture consisting of 42.0 to 52.0 mol%  $\text{Fe}_2\text{O}_3$ , 0 to 10.0 mol%  $\text{TiO}_2$  or  $\text{SnO}_2$  and the remainder shared with MnO and ZnO at a molar ratio of 26:25, which was made by mixing respective raw material powders, was calcined in the air at 900°C for 2 hours and milled with a ball mill for 20 hours to obtain mixed powder. Then, while the component of this mixed powder was adjusted so as to conform to the previously defined composition, CoO, NiO or MgO was added as additive in a prescribed amount to some of the mixed powder, which was further mixed with a ball mill for 1 hour. Then, this mixed powder with addition of polyvinyl alcohol was granulated and pressed at a pressure of 80 MPa into toroidal cores (green compacts) each having an outer diameter of 18 mm, an inner diameter of 10 mm and a height of 4 mm. The green compacts were put into a sintering furnace, then sintered at 1200°C for 3 hours and immediately cooled in an atmosphere adjusted by allowing nitrogen to flow therein so as to have such a relative partial pressure of oxygen as obtained with the constant b in the expression (1) set to 8, and samples 1-1 to 1-9 shown in Table 1 were obtained.

[0024] On the respective samples 1-1 to 1-9 thus obtained, final component composition was checked by the fluorescent X-ray analysis and electrical resistance was measured, and also initial permeability was measured at 0.1 MHz, 1 MHz, and 10 MHz. Their results are shown together in Table 1.

Table 1

Sample number	Classification	Basic component composition (mol %)				Additive (mass %)	Electrical resistance [ $\Omega\text{m}$ ]	Initial permeability		
		$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{ZnO}$	$\text{TiO}_2$	$\text{SnO}_2$		0.1MHz	1MHz	10MHz
1-1	Comparative example	52.0	24.5	23.5	-	-	0.16	3880	740	1
1-2	Comparative example	47.0	27.0	26.0	-	-	290	3960	940	70
1-3	Present invention	47.0	26.0	25.0	-	2.0	300	6170	2010	220
1-4	Present invention	47.0	26.0	25.0	5.0	-	380	6730	2000	230
1-5	Comparative example	47.0	26.0	25.0	2.0	-	410	3320	1150	150
1-6	Present invention	44.0	27.5	26.5	-	8.0	360	6600	2080	210
1-7	Comparative example	42.0	28.5	27.5	2.0	-	390	3720	1280	140
1-8	Present invention	50.0	25.4	24.5	0.1	-	200	6720	2020	200
1-9	Comparative example	47.0	21.9	21.1	-	10.0	440	3840	1190	130

[0025] As apparent from the results shown in Table 1, all samples 1-2 to 1-9 each having 50.0 mol% or less  $\text{Fe}_2\text{O}_3$  have remarkably high electrical resistances as compared to comparative sample 1-1 having  $\text{Fe}_2\text{O}_3$  exceeding 50.0 mol%. Further, among samples each having 50.0 mol% or less  $\text{Fe}_2\text{O}_3$ , samples 1-3, 1-4, 1-6 and 1-8 of the present invention, each containing 44.0 to 50.0 mol%  $\text{Fe}_2\text{O}_3$  and 0.1 to 8.0 mol%  $\text{TiO}_2$  or  $\text{SnO}_2$  as basic component composition and also containing 0.01 to 2.00 mass% CoO, NiO, or MgO as additive, could obtain a remarkably high initial permeability of 2000 or more at 1 MHz, and 200 or more even at 10 MHz. On the other hand, the initial permeability of comparative sample 1-1 is 1 at a frequency of 10 MHz, which indicates properties of soft magnetic material are totally lost.

#### Example 2

[0026] A mixture consisting of 47.0 mol%  $\text{Fe}_2\text{O}_3$ , 2.0 mol%  $\text{TiO}_2$  or  $\text{SnO}_2$ , 0 to 20.0 mol% CuO and the remainder shared with MnO and ZnO at a molar ratio of 26:25, which was made by mixing respective raw material powders, was calcined in the air at 900°C for 2 hours and milled with a ball mill for 20 hours to obtain mixed powder. Then, while the component of this mixed powder was adjusted so as to conform to the previously defined composition, the mixed powder with addition of 0.50 mass% CoO, NiO or MgO as additive was further mixed with a ball mill for 1 hour. Then, this mixed powder with addition of polyvinyl alcohol was granulated, and pressed at a pressure of 80 MPa into toroidal cores (green compacts) each having an outer diameter of 18 mm, an inner diameter of 10 mm and a height of 4 mm. The green compacts were put into a sintering furnace, then sintered at 900 to 1200°C for 3 hours and immediately cooled in an atmosphere adjusted by allowing nitrogen to flow therein so as to have such an oxygen concentration as obtained with the constant b in the expression (1) set to 8, and samples 2-1 to 2-4 shown in Table 2 were obtained.

[0027] On the respective samples 2-1 to 2-4 thus obtained, final component composition was checked by the fluorescent X-ray analysis, and also initial permeability was measured at 1 MHz. Their results are shown together in Table 2.

Table 2

Sample number	Classifi- cation	Basic component composition (mol %)						Additive (mass %)	Initial permeability at each sintering temperature		
		Fe <sub>2</sub> O <sub>3</sub>	MnO	ZnO	TiO <sub>2</sub>	SnO <sub>2</sub>	CuO		1200°C	1050°C	900°C
2-1	Present invention	47.0	26.0	25.0	2.0	-	-	0.50 (CoO)	2120	1530	820
2-2	Present invention	47.0	22.0	21.0	-	2.0	8.0	0.50 (NiO)	1590	2150	1610
2-3	Present invention	47.0	17.8	17.2	2.0	-	16.0	0.50 (MgO)	1160	1740	2030
2-4	Comparative example	47.0	15.8	15.2	2.0	-	20.0	0.50 (CoO)	560	980	1070

[0028] As apparent from the results shown in Table 2, in the case of sample 2-1 (of the present invention) containing no CuO, a sintering temperature must be set at as high as 1200°C to obtain a high initial permeability of 2000 or more. However, in the case of samples 2-2 and 2-3 (of the present invention) containing a suitable amount of CuO, a high initial permeability of 2000 or more could be obtained even when they were sintered at a temperature lower than 1200°C. On the other hand, in the case of sample 2-4 (comparative sample) containing a large amount (20.0 mol%) of CuO, the initial permeability was significantly lowered when it was subjected to sintering at a high temperature of 1200°C. Further, even when sintering was carried out at a temperature lower than 1200°C, a high initial permeability exceeding 2000 could not be obtained. Thus, it has been found that a suitable amount of CuO content works effectively for lowering the optimum sintering temperature and enhancing the initial permeability in a high frequency region.

### Example 3

[0029] A mixture consisting of 47.0 mol% Fe<sub>2</sub>O<sub>3</sub>, 2.0 mol% TiO<sub>2</sub> or SnO<sub>2</sub>, 0 to 8.0 mol% CuO and the remainder shared with MnO and ZnO at a molar ratio of 26:25, which was made by mixing respective raw material powders, was calcined in the air at 900°C for 2 hours and milled with a ball mill for 20 hours to obtain mixed powder. Then, while the component of this mixed powder was adjusted so as to have the previously defined composition, the mixed powder with addition of 0.50 mass% CoO, NiO or MgO as additive was further mixed with a ball mill for 1 hour. Then, this mixed powder with addition of polyvinyl alcohol was granulated and pressed at a pressure of 80 MPa into toroidal cores (green compacts) each having an outer diameter of 18 mm, an inner diameter of 10 mm and a height of 4 mm. The green compacts were put into a sintering furnace, sintered at 1200°C or 1050°C (1050°C only for the green compacts containing CuO) for 3 hours and immediately cooled in the air or in an atmosphere adjusted by allowing nitrogen to flow thereinto so as to have such a partial pressure of oxygen as obtained with the constant b in the expression (1) changed variously within a range of 5.5 to 21, and samples 3-1 to 3-8 shown in Table 3 were obtained.

[0030] On the respective samples 3-1 to 3-8 thus obtained, final composition was checked by the fluorescent X ray analysis and electrical resistance was measured, and also initial permeability was measured at 0.1 MHz, 1 MHz, and 10 MHz. Their results are shown together in Table 3.



Table 3

Sample number	Classifi- cation	Basic component composition (mol %)				Additive (mass %)	Constant b	Electrical resistance [ $\Omega$ m]	Initial permeability		
		Fe <sub>2</sub> O <sub>3</sub>	MnO	ZnO	TiO <sub>2</sub>	SnO <sub>2</sub>			0.1MHz	1MHz	10MHz
3-1	Comparative example	47.0	26.0	25.0	2.0	-	-	5.5	5820	940	80
3-2	Present invention	47.0	26.0	25.0	2.0	-	-	6.0	6930	2010	200
3-3	Present invention	47.0	26.0	25.0	-	2.0	-	8.0	6660	2060	210
3-4	Present invention	47.0	26.0	25.0	2.0	-	-	10.0	5230	2090	230
3-5	Present invention	47.0	21.9	20.0	-	2.0	8.0	16.0	3890	2140	220
3-6	Present invention	47.0	26.0	25.0	2.0	-	-	21.0	3340	2230	230
3-7	Present invention	47.0	26.0	25.0	-	2.0	-	in the air	2170	2480	240
3-8	Present invention	47.0	21.9	20.1	2.0	-	8.0	in the air	2410	2230	240

[0031] As apparent from the results shown in Table 3, samples 3-2 to 3-6 of the present invention which were sintered in an atmosphere with partial pressure of oxygen obtained by the expression (1) where the constant b is defined as 6 or more, and the samples 3-7 and 3-8 of the present invention which were sintered in the air both have a high electrical resistance. In accordance with this, the initial permeabilities at high frequencies of 1 MHz and 10 MHz are also increased. Among them, samples 3-7 and 3-8 of the present invention which were sintered in the air have a high electrical resistance and a high initial permeability in a high frequency region as compared to the samples which were sintered in different atmospheres. On the other hand, in comparative sample 3-1 which was sintered in an atmosphere with the partial pressure of oxygen obtained when the constant b is defined as 5.5, though the initial permeabilities at 0.1 MHz is high, the initial permeabilities at high frequencies of 1 MHz and 10 MHz are the lowest.

[0032] According to the Mn-Zn ferrite and the production process thereof described above in the present invention, with a unique component composition in which  $\text{Fe}_2\text{O}_3$  content is limited to 50 mol% or less by allowing  $\text{TiO}_2$  or  $\text{SnO}_2$  to be contained and in which CoO, NiO or MgO is contained as additive, an excellent initial permeability can be obtained in a wide frequency band from a comparatively low frequency region to a high frequency region of 10 MHz regardless of the Mn-Zn ferrite sintered in the air or in an atmosphere containing some amount of oxygen.

[0033] Further, according to the present invention, the troublesome atmosphere control is not necessary in sintering. Particularly, when the Mn-Zn ferrite contains CuO, it can be sintered at a low temperature and the cost for sintering is further reduced, which contributes significantly to cost reduction of the Mn-Zn ferrite.

## Claims

1. A Mn-Zn ferrite wherein a basic component composition contains 44.0 to 50.0 mol%  $\text{Fe}_2\text{O}_3$ , 4.0 to 26.5 mol% ZnO, 0.1 to 8.0 mol% at least one from  $\text{TiO}_2$  and  $\text{SnO}_2$  and the remainder consisting of MnO, and further contains 0.01 to 2.00 mass% at least one from CoO, NiO and MgO as additive.
2. A Mn-Zn ferrite wherein a basic component composition contains 44.0 to 50.0 mol%  $\text{Fe}_2\text{O}_3$ , 4.0 to 26.5 mol% ZnO, 0.1 to 8.0 mol% at least one from  $\text{TiO}_2$  and  $\text{SnO}_2$ , 0.1 to 16.0 mol% CuO and the remainder consisting of MnO, and further contains 0.01 to 2.00 mass% at least one from CoO, NiO and MgO as additive.
3. A production process of the Mn-Zn ferrite wherein mixed powder whose components are adjusted so as to have the composition of the Mn-Zn ferrite according to claim 1 or 2 is pressed, then sintered and immediately cooled in the air.
4. A production process of the Mn-Zn ferrite wherein mixed powder whose components are adjusted so as to have the composition of the Mn-Zn ferrite according to claim 1 or 2 is pressed, then sintered and immediately cooled down to 300°C maximum in an atmosphere with a partial pressure of oxygen defined by the following expression:

$$\log P_{\text{O}_2} = -14540/(T + 273) + b$$

where T: Temperature (°C),  $P_{\text{O}_2}$ : relative partial pressure of oxygen where  $P_{\text{O}_2} = \frac{P'_{\text{O}_2}}{P_{\text{total}}}$ ,  $P'_{\text{O}_2}$  is the absolute partial pressure of oxygen (Pa), and  $P_{\text{total}}$  is the absolute pressure (Pa), and b: a constant selected from a range of 6 to 21.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 00 12 5415

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	BHISES B V ET AL: "ROLE OF MNTI AND MNSN SUBSTITUTIONS ON THE ELECTRICAL PROPERTIES OFNI-ZN FERRITES" PHYSICA STATUS SOLIDI (A). APPLIED RESEARCH,DE,BERLIN, vol. 157, no. 2, 1 October 1996 (1996-10-01), pages 411-419, XP002056913 ISSN: 0031-8965 * page 411 *	1	C01G49/00 H01F1/34
A	EP 0 951 024 A (TDK CORP) 20 October 1999 (1999-10-20) * page 3; claim 1 *	1,2	
A	EP 0 844 220 A (NIPPON ELECTRIC CO) 27 May 1998 (1998-05-27) * the whole document *	1	
A	US 4 808 327 A (ROUSSET ABEL ET AL) 28 February 1989 (1989-02-28) * the whole document *	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	US 5 593 612 A (LUBITZ PETER) 14 January 1997 (1997-01-14) * the whole document *	1,2	C01G H01F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 February 2001	Examiner LIBBERECHT, E
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	

EPO FORM 1503 03.02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 12 5415

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-02-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0951024 A	20-10-1999	WO 9916090 A	01-04-1999
		JP 11163582 A	18-06-1999
EP 0844220 A	27-05-1998	JP 3003601 B	31-01-2000
		JP 9268052 A	14-10-1997
		US 5874020 A	23-02-1999
US 4808327 A	28-02-1989	FR 2587990 A	03-04-1987
		AT 48716 T	15-12-1989
		DE 3667563 D	18-01-1990
		EP 0240529 A	14-10-1987
		WO 8702173 A	09-04-1987
		JP 63501834 T	21-07-1988
US 5593612 A	14-01-1997	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82